Rapid Method For Distilling Fluorides From Water Samples

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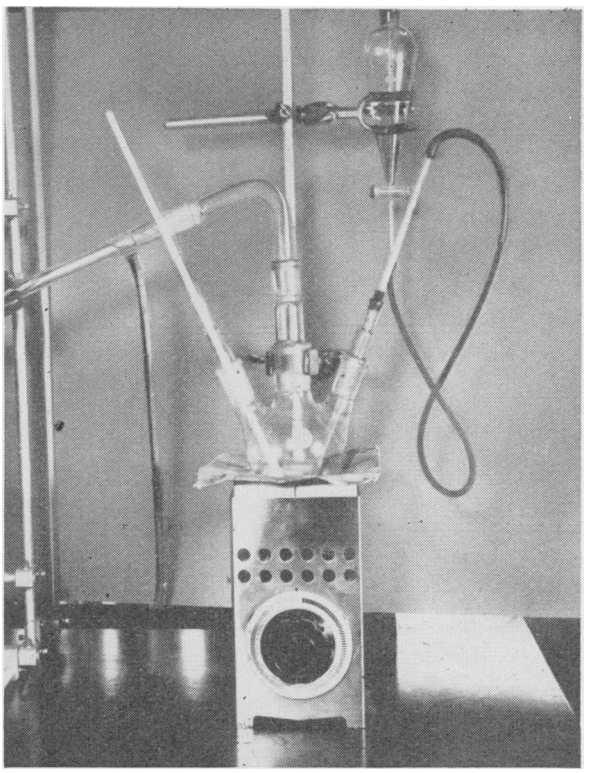
Distillation of fluorides from water samples, when concentration of the sample is unnecessary, may be made in less than 30 minutes, one-third of the time required for distillation by the standard method, by simply introducing the sample itself at a slow constant rate into a mixture of water and sulfuric acid kept boiling at a temperature of 140° C. Where frequent fluoride distillations are required, the timesaving features of this method make it particularly useful.

The method described here evolved from the logical supposition that with a constant distillation rate and temperature and with fluoride entering the flask in the sample water and leaving the flask in the distillate, the concentration of the fluoride in the distillate would eventually be the same as the concentration in the sample. The rate of distillation might have a slight effect on the point at which equilibrium is attained, but equilibrium must be reached at some point as long as the rate is constant.

Distilling Apparatus

The distilling apparatus used in the experimental work to be described is shown in the acompanying illustration. The flask is a 500-ml. three-necked boiling flask fitted with a thermometer which extends into the liquid being distilled. The sample lead-in tube is a 0.1-ml. pipette connected to a separatory funnel by a length of rubber tubing and fitted into one neck of the flask by means of a rubber sleeve. All other joints are standard taper glass. The separatory funnel has a notched stopcock for easy control of flow at slow rates; a glass tube fitted in a rubber stopper reaches nearly to the bottom of the funnel to provide a constant head of liquid. The heating unit is a 750-watt heater with transformer control.



Distillation apparatus used in experimental work on rapid method for distilling fluorides.

Procedure

The flask is charged with 15 ml. of sulfuric acid, glass beads, a small amount of silver sulfate, and sufficient water to give a boiling point of 138° to 140° C.

In making a distillation, the sample is introduced at a rate sufficient to maintain a temperature of 138° to 140° C. with the heating unit set at full capacity. With the apparatus described, distillation proceeds at the rate of approximately 7 ml. per minute. All tests described below are based on a distillation rate of 7 ml. per minute at 138° to 140° C.

At the end of one distillation, the excess sample in the separatory funnel is discarded and a new sample introduced, the lead-in tube to the flask being removed and flushed with the new

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sample. The separatory funnel and lead-in tube are again placed in position, and the distillation is restarted. The acid charge in the flask may be used repeatedly. As many as 20 distillations from one batch of acid have been made with no apparent difficulty. The frequency of acid renewal should probably depend upon the mineral and organic-matter content of the water analyzed.

Equilibrium Studies

Preliminary experiments were made with a known concentration of fluoride in distilled water in order to determine how rapidly equilibrium between input and output would be established. One hundred milliliters of distilled water were distilled through the apparatus and discarded. Then a solution containing 2 ppm fluoride was distilled, and five 50-ml. portions were collected. Distillation of the fluoride solution was discontinued and distilled water substituted, five 50-ml. portions again being collected.

The fluoride content of the portions collected and of all subsequent samples described in this report was determined by the Sanchis method, modified by Scott, as outlined in "Standard Methods for the Examination of Water and Sewage," ninth edition. Analysis of these samples gave the results in table 1, which indicate that for routine work distillation of 50 ml. to waste at the beginning of each new sample should be sufficient.

In order to determine whether or not equilibrium would be established at a similar rate with tapwater, fluoride was added to Minneapolis tapwater at the rate of 1.5 ppm. The apparatus was cleared of fluorides by distilling 300 ml. of distilled water through it. Then distillation of the fortified Minneapolis water was started, and four consecutive 50-ml. portions were collected. Results of the analysis of these portions, shown below, again indicate that for routine work a sufficiently adequate equilibrium is established after the distillation of 50 ml. to waste.

Table 1. Recovery of fluoride in successive 50-ml. portions

Portion No.	Concentration in feed (ppm)	Concentration in recovered distillate (ppm)
1	2	1.5
2	2	2
3	2	2
4	2	2
5	2	2
6	0	.7
7	0	.02
8	0	Trace
9	0	0
10	0	0

Portion No.	*Concentration in recovered distillate (ppm)*
1	1.00
2	1.56
3	1.58
4	1.59

Another series of experiments was made with Minneapolis tapwater to determine whether or not the distillation of 50 ml. to waste before collecting a sample would be sufficient for samples with a higher fluoride concentration. After the apparatus was cleared with distilled water, four successive 50-ml. portions were collected from distillate of Minneapolis tapwater containing 5 ppm added fluoride. Results of the analysis of these portions, shown below, indicate that equilibrium is established at approximately equal rates for samples containing about 1.5 ppm and 5 ppm fluoride.

Portion No.	*Concentration in recovered distillate (ppm)*
1	3.75
2	4.80
3	5.0
4	5.0

Accuracy Tests

Further experiments with tapwater were made to determine the general accuracy of the procedure as it would actually be used. Samples of Minneapolis tapwater containing 1.5 ppm added fluoride were alternated with samples of Minneapolis tapwater containing only the naturally occurring fluorides, 50 ml. of distillate being discarded at the beginning of each change. Both the distilled samples and the undistilled samples were analyzed by the standard method. Results of these tests, shown

Table 2. Recovery of fluoride from Minneapolis water—normal and fortified samples

Portion No.	Fluoride added (ppm)	Fluoride recovered (ppm)	
		Distilled	Not distilled
1 [1]	0	0.11	0.15
2	0	.12	
3	0	.11	
4 [1]	1.5	1.58	1.6
5 [1]	0	.10	
6 [1]	1.5	1.54	
7 [1]	0	.13	
8 [1]	1.5	1.56	

[1] 50 ml. of distillate discarded before collecting sample.

in table 2, indicate that the technique is sufficiently accurate for routine work.

Other Substances Added

It has been reported that aluminum may cause irregularity in the recovery of fluorides by distillation. Although waters in Minnesota usually contain less than 0.5 ppm aluminum, it was decided to investigate the effect of added aluminum. Test solutions were made by adding 1.5 ppm of fluoride and 10 ppm of aluminum to Minneapolis tapwater. Two hundred and fifty milliliters of this solution were distilled, the first 50 ml. being discarded and two successive 100-ml. portions collected. Then, 250 ml. of Minneapolis water containing 1.5 ppm of added fluoride were distilled, the first 50 ml. again being discarded and two 100-ml. portions collected. The results of the analysis of these samples are tabulated in table 3. There appears to be little or no effect on fluoride recovery either during the time the aluminum was being added or on samples distilled after 2.5 milligrams of aluminum had accumulated in the flask.

Table 3. Fluoride recovery from Minneapolis water in presence of aluminum

Portion No.	Aluminum added (ppm)	Fluoride added (ppm)	Fluoride recovered (ppm)
1 [1]	0	1.5	1.56
2 [1]	10	1.5	1.56
3	10	1.5	1.58
4 [1]	0	1.5	1.60
5	0	1.5	1.54

[1] 50 ml. of distillate discarded before collecting sample.

A similar experiment was made to determine the effect of dissolved silica on the distillation. Minneapolis water with 1.5 ppm added fluoride was distilled alternately with Minneapolis water containing 1.5 ppm added fluoride and 20 ppm added silica. The dissolved silica content of the original Minneapolis water was found to be 6 ppm by the molybdate colorimetric determination. Results of this experiment appear in table 4. No significant differences were found in fluoride recovery.

Table 4. Effect of silica on recovery of fluorides from Minneapolis water

Portion No.	Fluoride added (ppm)	Silica added (ppm)	Fluoride in distillate (ppm)
1 [1]	1.5	0	1.56
2	1.5	0	1.56
3 [1]	1.5	20	1.54
4	1.5	20	1.56
5 [1]	1.5	0	1.56
6 [1]	1.5	20	1.56
7	1.5	20	1.56
8 [1]	1.5	0	1.56

[1] 50 ml. of distillate discarded before collecting sample.

Conclusion and Summary

The distillation method outlined, which requires less than 30 minutes, appears to be sufficiently accurate for routine work. Equilibrium studies have shown that at a distillation rate of 7 ml. per minute and a temperature of 138° to 140° C., distillation of 50 ml. to waste at the beginning of each new sample is sufficient. The addition of aluminum and of dissolved silica to the test samples does not appear to affect significantly the recovery of fluoride from the distillate.

In Departmental Periodicals . . .

OCCUPATIONAL HEALTH

Training of Health Workers In Los Angeles Program

In the June 1953 issue of Occupational Health, Jack C. Rogers notes that public health personnel have generally refrained from entering the field of industrial hygiene.

The occupational health services in Los Angeles have been confined to the division of occupational health (which Mr. Rogers directs) in the city health department. To compensate for the manpower shortage within the division and still provide adequate health services throughout the city's sprawling area, other departmental personnel are being brought into the industrial health program. This is being achieved with the cooperation of the other administrative units of the city health department.

As a result of the program, sanitarians and public health nurses are getting training and technical guidance in their jobs from the division of occupational health. Similarly, sanitarians are training industrial hygienists in industrial sanitation. Public health nurses are being trained to act as contacts between industry and the division of occupational health. Both are being alerted to spot and report to the health department the occupational hazards they uncover.

Mr. Rogers points out that by the actual designation of the occupational health division as the one unit of the department which is responsible for all contact with industry, the danger of overlapping or conflict in plant inspections or in instructions is eliminated. The division thereby handles all matters involving industry from those problems normally assigned to the occupational health program to those connected with water supplies, cross connections, industrial wastes, and others.

Michigan Training Program In Industrial Hygiene

The need for the control and prevention of occupational disease was recognized as early as 1875 in Michigan, according to John C. Soet, chief of Michigan's division of industrial health. The entire field of official industrial hygiene is faced with the twofold problem of keeping the small total of experienced personnel at its present level and of having some satisfactory source of replacement.

Finding that its entrance requirement of a year's experience in industrial health was losing potential candidates for careers in industrial health, the Michigan Department of Health now offers a training program for graduate engineers and other qualified applicants. This program is designed particularly to attract graduates in chemical engineering to the profession of public health engineering.

The training program combines field work with classroom and lecture sessions over a 23-week period. It now includes a special ventilation conference at Michigan State College, special industrial health conferences at the Michigan School of Public Health and will include the radiological health course offered by the Public Health Service. Trainees do not assume any real responsibility for the first 2 years but work under the supervision of experienced men.

"Our statistics show that over the years the vast majority do remain in industrial hygiene," Mr. Soet stated, adding that, on the average, the trainees remained for a long period of time—long enough to repay the cost of training.

Suspension Notice

Publication of *Occupational Health*, a monthly since 1940, has been suspended with its July 1953 issue as the result of reduction in appropriations. However, *Public Health Reports*—which in recent issues has presented papers on air pollution, human relations in industry, occupational and environmental aspects of various diseases, and industrial dentistry—will give increased attention to technical topics in occupational health. Official agencies, professional organizations, and teaching institutions not now receiving *Public Health Reports* should inquire of the Public Health Service as to their eligibility for official or free subscriptions. Other groups—and individuals wishing personal copies—should purchase subscriptions. *Use the subscription blank on the inside back cover of this issue.*

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